

(12) UK Patent Application (19) GB (11) 2 367 108 (13) A

(43) Date of A Publication 27.03.2002

(21) Application No 0118275.7

(22) Date of Filing 26.07.2001

(30) Priority Data
(31) 09631024 (32) 02.08.2000 (33) US

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(51) INT CL⁷
F16L 9/14 9/12 11/14

(52) UK CL (Edition T)
F2P PC12 PC26 P1B7A P1B7B P1B7C P1B7D P1B7F
P1B7P

(56) Documents Cited
GB 2048427 A US 6071579 A
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(58) Field of Search
UK CL (Edition T) F2P PC12 PC13 PC26 PC27 PC29
INT CL⁷ F16L 9/12 9/14 11/00 11/04 11/12 11/14
ONLINE: WPI, EPDOC, JAPIO

(54) Abstract Title
Laminated nylon air brake tubing

(57) A laminated nylon air brake tubing is formed from outer and inner layers of nylon 11 or nylon 12 with inner layers of nylon 6. The nylon 6 and nylon 11 or 12 layers are adhered together by a tie layer. The tie layer is preferably a nylon 6-12 or an anhydride modified polyolefin. The air brake tubing has improved high temperature strength and low temperature impact resistance characteristics.

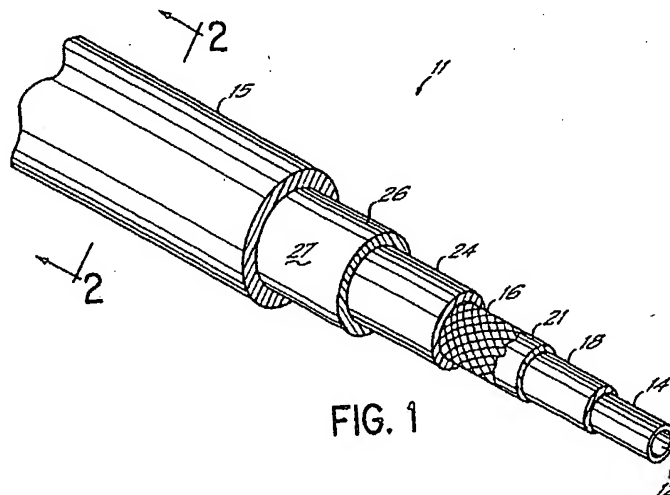
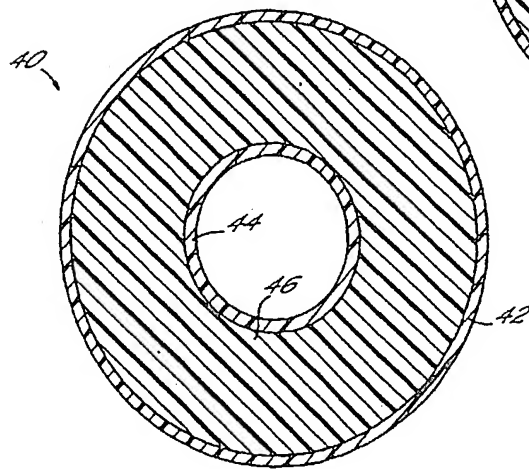
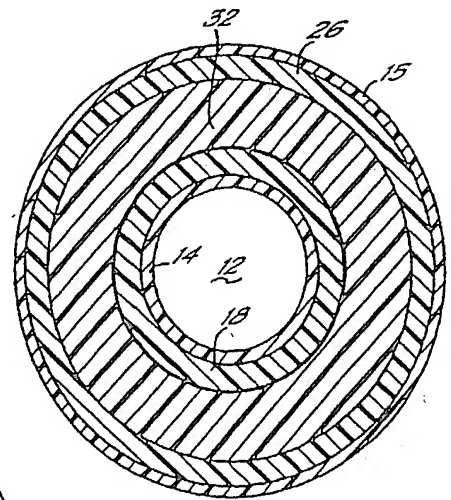
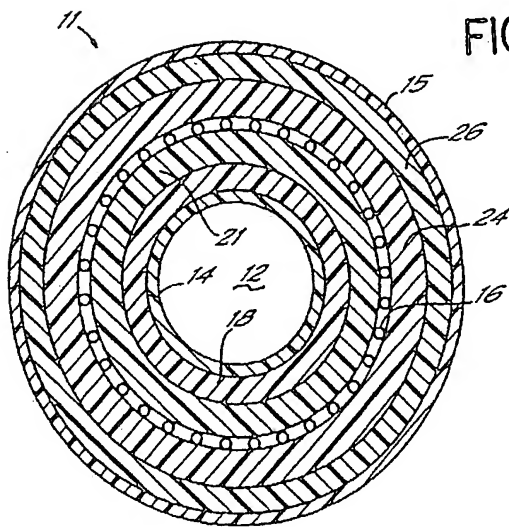
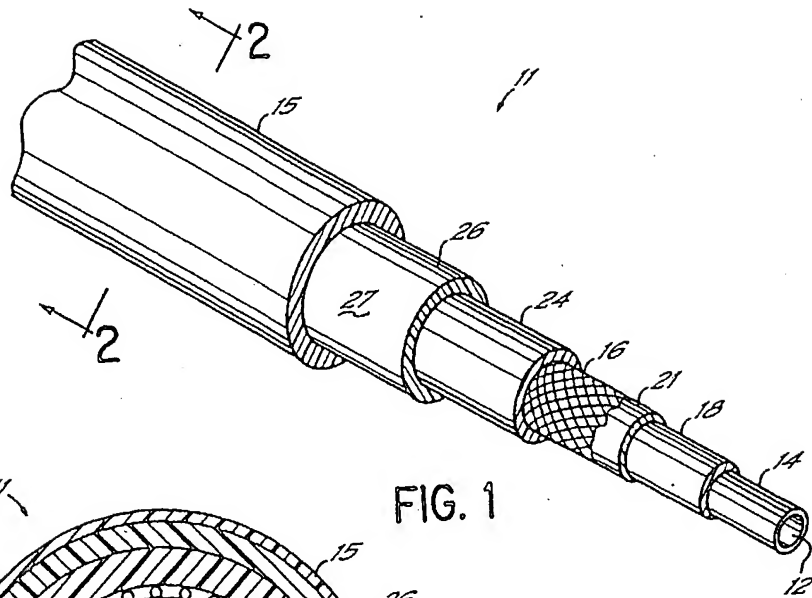


FIG. 1

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Laminated Nylon Air Brake Tubing

5 Air brake systems are frequently employed in heavy duty vehicles such as tractor trailers and the like. In such systems the brake system is activated by pressurized air transported through tubing. Metal tubing can be employed, however nylon tubing is generally preferred and specifically polyester reinforced nylon tubing. Nylon tubing such as disclosed in Brumbach, U.S. Patent 3,062,241 has met with exceptional success and has been established as the industry standard.

10 This product includes a nylon 11 or 12 inner and outer layer separated by an intermediate polyester fiber layer. The inner and outer layers are laminated securely together and do not delaminate under operating conditions typically up to 150 psi over a wide temperature range i.e., from -40 to 200°F. Further nylon 11 and nylon 12 are well suited for
15 automotive and truck applications. Their resistance to cracking and their fuel and water resistance are exceptional. Further they are not sensitive to stress cracking from zinc chloride as is nylon 6.

Nylon 11 and 12 present some concerns. In particular the cost and availability of these products is a concern. Nylon 11 is only manufactured by one company. Nylon 12 is made by four. Further nylon 11 and 12 are unsuitable for use in temperatures below -40°F or extremely high temperatures i.e., higher than 200°F. In Europe, if resistance to higher temperatures is required, manufacturers typically utilize nylon 6. This is less expensive than nylon 11 and 12. But at low temperatures i.e., about -40°F, the unmodified nylon 6 tends to be brittle in cold impact.

Nylon 6 is also subject to stress cracking when contacted with zinc chloride and loses physical properties when saturated with water. Zinc chloride resistance is a problem in certain environments particularly where road salt is used to melt ice and snow or near the ocean. Many hose connectors are zinc plated and when contacted with sodium chloride from salt spray and the like, form zinc chloride which causes nylon 6 to break down. For this reason nylon 6 has not been accepted for use in the United States and is only used in limited applications in other countries.

Further nylon 6 per se is not compatible with nylon 11 or 12 and thus forming a laminated tubing using layers of nylon 11 or 12 is problematic. Until now because of the application requirements and compatibility requirements, laminated tubing from nylon 6 and nylon 12 or nylon 11 have not been feasible.

Summary of the Invention

The present invention is premised on the realization that laminated reinforced nylon air brake tubing can be formed from layers of nylon 11 or 12 and nylon 6 or nylon 6-6 by incorporating an adjacent layer and at the same time utilizing modified nylon 6 or nylon 6-6. In one preferred embodiment an intermediate tie layer is employed which is a nylon 6-12 or a maleic anhydride modified polyolefin which is compatible with nylon 6, nylon 6-6 and nylon 11 or nylon 12 and in particular compatible with even the modified nylon 6 or nylon 6-6.

By utilizing a modified nylon 6 or 6-6, the disadvantages of nylon 6 are reduced and at the same time it remains compatible with the tie layer. By utilizing inner and outer layers of nylon 11 or 12, the threats to nylon 6 from environmental concerns including moisture and zinc chloride are eliminated and further this is all accomplished while retaining the high temperature advantages of nylon 6 or 6-6.

The invention will now be further described by way of example only with reference to the accompanying drawings in which:

Fig. 1 is a perspective view partially broken away of air brake tubing of the present invention.

Fig. 2 is a cross-sectional view taken at lines 2-2 of Fig. 1.

Fig. 3 is a cross-sectional view of an alternate embodiment of the present invention.

Fig. 4 is a cross-sectional view of a second alternative embodiment of the present invention.

5 Air brake tubing 11 shown in Figs. 1 and 2, includes
an inner layer 14 and an outer layer 15 which defines
a hollow interior area 12. Both the outer layer 15 and the inner layer 14
are formed from either nylon 11 or 12. Intermediate the inner layer 14
10 and outer layer 15 is at least one layer of nylon 6 or nylon 6-6 which is
separated from the inner and outer layers 14 and 15 by tie layers. Inner
layer 14 is optional and can be eliminated to reduce cost

More particularly with respect to the embodiment shown in Fig. 1,
the tubing includes innermost layer 14 bonded to a tie layer 18 bonded to
15 a modified nylon 6 or 6-6 layer 21. Layer 21 is surrounded by a fiber layer
or braiding layer 16. A second nylon 6 or 6-6 layer 24 surrounds the
braiding 16 and in turn tie layer 26 connects the outer nylon layer 15 to
layer 24.

Layers 14 and 15 are either nylon 11 or nylon 12. It is preferable
20 to have these layers as thin as possible and generally outer layer 15 will
be in the neighborhood of 0.005 to 0.015 inches thick preferably 0.007
inches. Inner layer 14 is preferably .001 to 0.005 inches preferably .002.

The purpose of these layers is to provide isolation from the automotive environment such as moisture and ZnCl as well as others.

5 The nylon 11 and 12 layers are made from commercially available plasticized polyamide such as Rilsan BESNO p40 TL 89 (Nylon 11) or optionally plasticized nylon 12 which can be purchased from Huls under the brand name X7293 or Rilsan AESNO p401 TL. Alloys of nylon 11 and/or nylon 12 can also be employed. These alloys are simply nylon blended with less than 50% by weight of a compatible polymer such as maleic anhydride modified high density polyethylene. Hereinafter the
10 term nylon 11 or 12 is intended to include both 100% nylon as well as comparably performing nylon blends.

The tie layers 26 and 18 are again preferably as thin as possible and are formed from a 0-100% nylon 6 12 blended with 0-100% maleic anhydride modified polyolefin. Nylon 6-12 is manufactured by Dupont
15 sold as FE3646 or Huls B50565. This product may be used without further formulation but can be modified by the addition of plasticizer and impact modifiers. The maleic anhydride modified polyolefin is sold by Dupont as Fusabond 100D. The thickness of the tie layers 26 and 18 should be from 0.001 to 0.005 inches preferably 0.002 inches. The nylon
20 6-12 is preferred because its upper temperature limit is about 300°F. Preferably 95% to 100% nylon 6-12 is employed.

The Nylon 6 or 6-6 layer 21 generally has a thickness of .020 to about .030 preferably .025. Layer 24 is preferably .029 to .044 and

preferably .035 inches thick. These layers provide the primary structural support for the tubing. Therefore their thickness is determined by application requirements.

5 The nylon 6 or nylon 6-6 is modified to provide improved low temperature characteristics by blending the nylon with suitable impact modifiers to improve these characteristics. Preferably the nylon 6 or 6-6 will include 5-15% of a compatible impact modifier such as a compatible elastomer. Suitable impact modifiers include maleic anhydride modified EPDM and styrene butadiene rubber.

10 The Nylon 6 or 6-6 may have the following physical characteristics:

Ambient flex modulus 40,000-100,000 psi preferably 85,000 psi

Elastic modulus @ 230F 10,000-40,000 psi preferably 20,000 psi

Yield strength @ 230F 1000-2000 psi preferably 1500 psi

15 Izod impact strength @-70C .7-2.0 preferably 1.6

A preferred Nylon 6 formula includes:

High molecular weight (63%) Nylon 6 base resin

Plasticizer - butyl benzene sulfonamide 10-16% preferably 14%

Residual Nylon monomer - caprolactam 5-10% preferably 7%

20 Maleic anhydride modified ethylene/propylene/non-conjugated diene elastomer 5-15% preferably 10% (Uniroyal Royaltuf 498)

Maleic anhydride modified polyethylene 2-8% preferably 5% (Dupont Fusabond 493)

25 Suitable heat and light stabilizers nominally 1%.

The reinforcing or braiding layer 16 comprises strands of polymeric fibers and preferably polyester fibers. The strands have a weight of from

500 to 1,000 denier with 840 denier being preferred. Commercially available polyester fiber is sold by Hoechst Celanese under the designation 840/70/VAR. Although polyester is preferred and generally accepted, any strengthening fiber can be used such as nylon, rayon and aramid fibers.

To form the tubing 11, the inner nylon tube 14 is co-extruded along with the tie layer 18 and the first nylon 6 or 6-6 layer 21. The melt temperature of the nylon extruder should be from 450°F to about 460°F preferably about 450°F.

The braiding 16 is then applied over the first nylon 6 or 6-6 layer 21 by passing the three layer extruded tubing through a braider or fiber reinforcing apparatus. The reinforcing material may be braided, knitted or spirally wrapped wherein one strand of the material is applied in a pitch in one direction and another strand is applied over the first with a pitch in the opposite direction. The braider is preferably a counter rotating fiber reinforcing device. Preferably the braided layer is applied with six bobbins of fiber applied at from two to five picks per inch, preferably three picks per inch.

Once the braiding is applied, the outer three layers are co-extruded over the inner tubing in the same manner as the first three layers at the same temperatures. The formed tubing is then passed through a cooling bath. The resulting extruded product has an outer diameter of about .125 to about .75 inches and is ready for use.

As a test a laminated hose was formed with

layer 1 being the innermost layer:

- 5 Layer 1-Nylon 11, 0.007 in. Huls X7293
- Layer 2-Nylon 6-12 0.002 in. Dupont FE3646
- Layer 3-Nylon 60.2 in (above formulation)
- Layer 4-Polyester fiber - 840 denier
- Layer 5-same as layer 3
- Layer 6-same as layer 2
- Layer 7-same as layer 1

10 This structure was compared to polyester fiber reinforced Nylon 11 tubing and Nylon 12 tubing.

High temperature and pressure performance were tested according to SAE 1131 which requires that the tubing withstands 450 psi for (5) minutes at 200°F. Both Nylon 11 and the improved composite
15 product satisfied this requirement.

The test was then extended by raising the pressure until failure occurred. The Nylon 11 product failed as the pressure was increased and would not withstand 550 psi. The composite product withstood 600 psi for 5 min.

20 In another special high temperature comparison test, both products were pressurized to 150 psi and the temperature raised until failure, holding the temperature a minimum of one hour at each point.

The Nylon 11 product failed at 310°F.

The Nylon composite product did not fail at 340°F.

25 These samples and samples of nylon 12 tubing were also subject to a cold impact testing. The results are shown in Table I.

Cold Impact Testing Below -40F SAE J844 Requirement	5/8/2000	Comparison of composite nylon air brake product versus nylon 11 & 12 All testing done on 1/4" size SAE dimensional product. (20 samples) results gives average burst v		
		SPEC REQUIREMENT	Nylon 11 TEST RESULTS	Nylon 12 TEST RESULTS
		No Fractures	no failures 1005 psi	no failures 1153 psi
		80% min burst after impact	11 failures in 20 samples	7 failures in 20 samples
		760 psi min	Not Tested	Not Tested
TEST DEFINITION				Composite 6/12 nylon TEST RESULTS
SAE Cold Temperature Impact @ -50F				no failures 1254 psi
SAE Cold Temperature Impact @ -60F				Not Tested
SAE Cold Temperature Impact @ -65F				no failures 1230 psi

These tests demonstrate the superior properties of the laminated tubing described herein.

Fig. 3 shows an alternate embodiment wherein the fiber layer 16 is not employed. Thus only one nylon 6 or 6-6 layer 32 is formed separated from the inner nylon layer 14 and the outer nylon layer 15 by tie layers 26 and 18 respectively. Again these would be the same compositions previously discussed. This can be co-extruded in one step.

Surprisingly manufacture of air brake tubing having a structure as shown in Fig. 4 is possible. The nylon 6-12 provides adequate cold impact strength as well as zinc chloride resistance to permit the elimination of the inner and outer nylon 11 or 12 layers of the embodiments shown in either Fig. 2 or Fig. 3. Thus, as shown in Fig. 4, the tubing 40 includes inner and outer nylon 6-12 layers 42 and 44 respectively which sandwich an intermediate thicker layer 46 of nylon 6 or nylon 6-6. The thickness of layer 42 can be from .0002 inches up to about .15 inches although it is preferred to keep it as thin as possible. The inner nylon 6-12 layer 44 is not necessary in all applications. When used, it will have a thickness of about .0002 to about 0.1 inches.

Thus due to the compatibility of the nylon 6-12 and the combined functional characteristics of the laminated tubing itself, nylon 11 and nylon 12 can be completely eliminated from air brake tubing.

Thus the present invention provides a less expensive laminated air brake tubing while at the same time improving the high temperature strength of the tubing. Finally the tubing itself is not subject to delamination even at elevated pressure and temperature.

CLAIMS

1. Air brake tubing comprising an outermost first layer bonded to a second layer in turn bonded to a third layer;

wherein said first layer is selected from the group consisting of Nylon 11, Nylon 12 and alloys thereof; and

said third layer is selected from the group consisting of impact modified Nylon 6 and impact modified Nylon 6-6; and

wherein said second layer is a tie layer compatible with said first and said third layers.

2. The air brake tubing claimed in claim 1 further comprising a fourth layer bonded to said third layer, a fifth layer bonded to said fourth layer wherein said fourth layer is a fiber reinforcing layer and wherein said fifth layer is selected from the group consisting of impact modified Nylon 6 and impact modified Nylon 6-6.
3. The air brake tubing claimed in claim 2 further comprising a sixth layer bonded to said fifth layer comprising nylon 6-12.
4. The air brake tubing claimed in claim 2 further comprising the sixth layer and a seventh layer wherein said seventh layer comprises a nylon selected from the group consisting of nylon 11, nylon 12 and alloys thereof and wherein said sixth layer bonds said seventh layer to said fifth layer and comprises a tie layer compatible with said fifth and seventh layers.
5. The air brake tubing claimed in claim 4 wherein said sixth layer and said fourth layer are selected from the group consisting of nylon 6-12, maleic anhydride modified polyolefins and blends thereof.
6. The air brake tubing claimed in claim 4 wherein said second layer and said sixth layer comprise nylon 6-12 and blends thereof and wherein said first layer and said seventh layer are formed from the same material.

7. The air brake tubing claimed in claim 1 wherein said second layer comprises impact modified nylon 6.

8. The air brake tubing claimed in claim 7 wherein said impact modified Nylon 6 has an ambient flex modulus of at least about 40,000, an elastic modulus at 230°F of at least 10,000, a yield strength at 230°F of 1,000 and an Izod impact strength at -70°C of at least .7.

9. Air brake tubing comprising a first outermost layer adjoining a second layer, adjoining a third layer, adjoining a fourth layer adjoining a fifth layer;

wherein said first layer is a nylon selected from the group consisting of nylon 11, nylon 12 and alloys thereof; and

said second layer comprises a tie layer compatible with said first and third layers;

said third layer comprises an impact modified nylon 6 having an ambient flex modulus of at least 40,000 and an elastic modulus at 230°F of at least 10,000, a yield strength at 230°F of at least 1,000 and an Izod impact strength of at least 70° of at least .7; and

wherein said fourth layer is the same as said third layer and wherein said fifth layer is the same as said first layer.

10. The air brake tubing claimed in claim 9 wherein said tie layer is selected from the group consisting of nylon 6-12, maleic anhydride modified polyolefins and blends thereof.
11. The air brake tubing claimed in claim 9 wherein said nylon 6 is elastomer modified nylon 6.
12. The air brake tubing claimed in claim 11 wherein said nylon 6 includes from about 5 to about 15% by weight of an elastomer.
13. The air brake tubing claimed in claim 12 wherein said elastomer is a maleic anhydride modified ethylene/propylene non-conjugated dien elastomer.

14. Air brake tubing comprising an outermost first layer adjacent, a second layer adjacent, a third layer adjacent, a fourth layer adjacent, a fifth layer adjacent, a sixth layer;

wherein said first layer is selected from a group consisting of nylon 11, nylon 12 and alloys thereof;

wherein said third layer comprises impact modified nylon 6;

wherein said second layer comprises a tie layer selected from the group consisting of nylon 6-12, compatibilized polyolefin and blends thereof;

wherein said fourth layer comprises a fiber reinforcing layer;

wherein said fifth layer is the same as said third layer; and

wherein said sixth layer is the same as said second layer.

15. The air brake tubing claimed in claim 14 further comprising an innermost seventh layer said innermost seventh layer comprising a nylon selected from the group consisting of nylon 11, nylon 12 and alloys thereof.

16. An air brake tubing comprising an outer layer of nylon 6-12 and a second inner layer adhesively bonded to said outer layer said second inner layer selected from the group consisting of impact modified nylon 6 and impact modified nylon 6-6.

17. The air brake tubing claimed in claim 16 further comprising an innermost layer of nylon 6-12 adhesively bonded to an inner surface of said second layer.
18. The air brake tubing claimed in claim 16 wherein said first layer has a thickness from about .0002 to about .15 inches.
19. The air brake tubing claimed in claim 16 further comprising a fiber reinforcing layer adjacent an inner surface of said second layer and a third layer adhesively bonded to said second layer said third layer selected from the group consisting of impact modified nylon 6 and impact modified nylon 6-6.
20. The air brake tubing claimed in claim 19 further comprising an innermost nylon 6-12 layer bonded to said second nylon 6 layer.
21. Air brake tubing substantially as described herein and illustrated in the accompanying drawings.



INVESTOR IN PEOPLE

Application No: GB 0118275.7
Claims searched: 1 to 8

Examiner: Damien J Huxley
Date of search: 16 January 2002

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): F2P: PC12, PC13, PC26, PC27, PC29

Int Cl (Ed.7): F16L: 9/12, 9/14, 11/00, 11/04, 11/12, 11/14

Other: ONLINE: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2048427 A (AUTOMOTIVE PRODUCTS) see lines 84 to 108 of the first page and the figures.	1
A	US 6071579 (GREEN) see the figure and from line 9 of page 2	
X	US 5076329 (BRUNNHOFER) see the whole document	1 and 2
A	US 4881576 (KITAMI) see the figures and lines 9 to 68 of column 2 in particular.	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.